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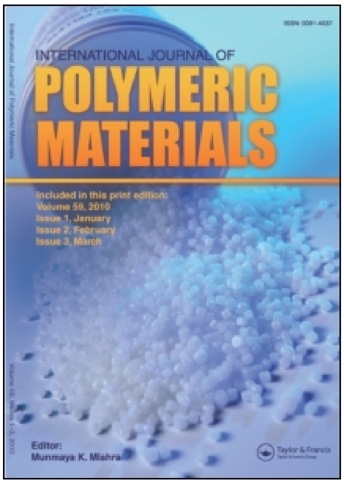

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Block-copolymers with Polyphenyl-α-Naphtylsilane Fragments in Dimethylsiloxane Chain

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Block-copolymers with Polyphenyl-α-Naphtylsilane Fragments in Dimethylsiloxane Chain

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The Wurtz-type reductive-coupling reaction of dichlorophenyl-α-naphtylsilanes was carried out both in the presence of metalic sodium in toluene solution and in a mixture of toluene and *o*-xylene (at 1:1 ratio) in the presence of sodium and catalytic amount of mercury. Oligomers of α,ω-dichlorophenyl-α-naphtylsilane with various degrees of polymerization were obtained. By hydrolysis of α,ω-dichlorophenyl-α-naphtylsilane the corresponding α,ω-dihydroxydiorganosilanes has been obtained. The heterofunctional condensation of α,ω-dichloro(dihydroxy)phenyl-α-naphtylsilanes with α,ω-dihydroxy(dichloro)dimethylsiloxanes in the presence of acceptor pyridine has been carried out and polysilane – siloxane block-copolymers were obtained. Depending on the lengths of the rigid and flexible initial oligomers microdomain structure of block-copolymers were observed. The synthesized block-copolymers were characterized by gel permeation chromatography, differential scanning calorimetry and X-ray methods.

Keywords: Polysilane; Thermal-oxidative stability; Block-copolymers

INTRODUCTION

The usual synthesis of polysilanes is by Wurtz-type reductive-coupling condensation of diorganodichlorosilanes with finely-divided sodium

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metal in an inert diluent. Both homopolymers and coplymers can be made [1]. The organic groups can be widely varied, to include alkyl, aryl and substituted organic groups, so that the polysilanes are a large, indeed infinite, class of new polymeric materials, which may be applied as photoresist materials [2], photoconductors [3], photoinitiators in radical polymerization [4] and as a ceramic precursor [5]. As is known from the literature [6], the reaction leading to the formation of polysilane polymers appears to be complex. Condensation may take place partly at or near the sodium surface and partly in solution. With excess sodium the polymers may be converted mainly to anionicaly-terminated, living polymer. These anionic ends will catalyze olefin polymerization [7], as well as polysilane–silane copolymers [8]. In all cases cyclic or linear oligomers are formed along with high polymers and ideed in many instances the oligomers are the dominant products. The yield and molecular weight distribution (MWD) of the polymers can be greatly influenced by bulk solvent effects, by the nature of the sodium dispersion and by the rate and order of addition [9]. The condensation reaction is usually carried out above the melting point of sodium, but some dichlorosilanes can be condensed to polymer by sodium dispersion near room temperature using ultrasound activation [10].

Polydimethylsilane and other polysilanes with very small alkyl substituents are highly crystalline and insoluble. By the replacement of methyl pendant groups with phenyl ones, the softening point of polymers rises and it flows only at temperatures > 200°C. Molecular weight distribution of polysilanes are frequently bi-or threemodal [11]. In the literature there is some information about the synthesis of polysilanes in the presence of sodium amalgam, but there is no information about the MWD and molecular masses of the synthesized polymers. Wurtz-type reaction has been carried out. By the authors [12], in the presence of metalic sodium with catalytic amount of mercury containing salts or metalic mercury (ratio 3:2) in a solution of toluene and *o*-xylene. Interesting results have been obtained in case when metalic mercury was used. In this case polysilanes with monomodal MWD and high MM were obtained.

EXPERIMENTAL PART

The starting materials α,ω-dihydroxydimethylsiloxanes with various length of the links were synthesized by a well-known method [13].

The organic solvents were purified by drying and distillation. The purity of the starting compounds was controlled by gas–liquid chromatography "ЛХМ-8 МД", phase SKTF-100 (10%), the NAW chromosorb, carrier gas-He, and 2 M column.

IR spectra of the synthesized compounds have been taken on an UR-20 instrument and ^{1}H NMR spectra on a Perkin-Elmer instrument at frequency operating frequency of 250 MHz, in solution of $C_2D_2Cl_4$ or $CDCl_3$.

X-ray diffraction patterns were taken on a "ДРОН-2 М" instrument, A-Cu_α values were measured without a filter, the angular velocity of the motor $\omega = 2$ deg/min.

Gel permeation chromatography was carried out using a Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastyragel columns. Sample concentrations were approximately 3% by weight in toluene, and typical injection volume for the siloxane was 5 μL. Standartization of the GPC was accomplished by the use of styrene or PDMS standards with known molecular weight.

The DSC analysis were carried out on a Perkin-Elmer instrument with temperature rise or decrease rate $\nu = 10$ deg/min.

Synthesis of α,ω-dichlorophenyl-α-naphtylsilanes

The Wurtz-type polycondensation reaction was carried out in a three-necked flask equipped with a reflux condenser, inert gas carrier tube and mechanical stirrer. A solution of 30,5 g (0,1 mole) of dichloro-phenyl-α-naphtylsilane in 35 ml dry toluene and 4,6 g sodium was refluxed until the sodium dissolved. After that the reaction mixture was filtered, the solution was concentrated and reprecipitated by using dry hexane.

The typical synthesis reactions of α,ω-dichlorophenyl-α-naphtylsilanes were carried out by the above mentioned method.

Synthesis of α,ω-dihydroxyphenyl-α-naphtylsilanes

The hydrolysis reaction was carried out in a three-necked flask equipped with reflux condenser dropping funnel and mechanical stirrer. To a solution of 0,22 g (0,0052 mole) sodium hydroxide, 40 ml water and 30 ml benzene in the temperature range $0 \div -5$°C, a solution of 10 g (0,0026 mole) α,ω-dichlorophenyl-α-naphtylsilane ($m \approx 15$) in 100 ml benzene was added. After that the reaction mixture was stirred at room temperature for 2 hours, was washed until neutral, dried above anhydrous Na_2SO_4, and the benzene removed by vacuum. The dihydroxy containing oligomer was reprecipitated from concentrated solution by using methyl alcohol, and 8,0 g (87%) α,ω-dihydroxyphenyl-α-naphtylsilane ($m \approx 15$) were obtained.

The typical synthesis reactions of α,ω-dihydroxyphenyl-α-naphtylsilanes were carried out by the above mentioned method.

Heterofunctional Condensation of α,ω-dichlorophenyl-α-naphtylsilanes ($m \approx 20$) with 1,3-dihydroxytetramethyldisiloxane

The polycondensation reaction was carried out in a three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. To a solution of 2,7981 g (5,939 mmole) α,ω-dichlorophenyl-α-naphtylsilanes in 2,5 ml anhydrous toluene at room temperature, a solution of 0,0986 g (5,939 mmole) 1,3-dihydroxytetramethyldisiloxane and 0,0939 g (11,878 mmole) pyridine in 0,5 ml anhydrous toluene was added. The mixture was stirred and heated for 5 hours at the boiling temperature of toluene. After that 8 ml of toluene were added and then filtered of and reaction mixture was washed from the traces of pyridine hydrochloric acid complex, dried above anhydrous Na_2SO_4, part of the toluene removed and reprecipitated by using methyl alcohol. 2,6 g (92,8%) copolymer XIX were obtained.

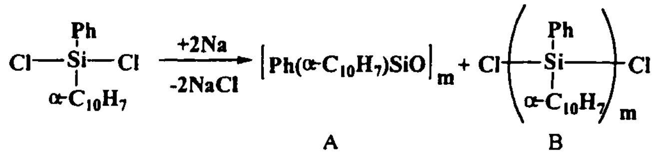
Typical synthesis reactions of other copolymers were carried out by the above mentioned method.

RESULTS AND DISCUSSION

In the literature there is some information about phenyl-α-naphtylsiloxane-dimethylsiloxane block-copolymers [14], where it was shown that the occurrence of block structure (phase incompatibility) in the copolymers is associated with the lengths of rigid phenyl-α-naphtylsiloxane and flexible dimethylsiloxane fragments. But there is no information about phenyl-α-naphtylsilane-dimethylsiloxane block-copolymers. Because of that we found it interesting to synthesize, new polyphenyl-α-naphtylsilane type oligomers by Wurtz-type reductive-coupling condensation with a different degrees of condensation, and to synthesize phenyl-α-naphtylsilane-dimethylsiloxane block-copolymers, on the basis of α,ω-dichloro(dihydroxy)phenyl-α-naphtylsilane by the reaction of heterofunctional condensation (HFC) with α,ω-dihydroxy(dichloro)dimethylsiloxanes.

For the purpose of synthesis of α,ω-dichlorophenyl-α-naphtylsilanes with a varying degrees of condensation, the Wurtz-type reaction was carried out by two ways. 1. The reaction of condensation of dichlorophenyl-α-naphtylsilane in the presence of metalic sodium (at the 1 : 1,5 or 1 : 1,8 ratio) was carried out in anhydrous toluene solution and in this case α,ω-dichlorophenyl-α-naphtylsilanes with a small degree of condensation has been obtained (oligomers I and II). 2. For the synthesis of α,ω-dichlorophenyl-α-naphtylsilanes with monomodal molecular weight distribution (MWD) and higher degree of conversion, the condensation of dichlorophenyl-α-naphtylsilane in the presence of various ratio (1 : 1,8 or 1 : 2), of metalic sodium in the mixture of toluene and *o*-xylene (at 1 : 1 ratio), in the presence of a catalytic amount of mercury has been carried out by a well-known method [12]. The mole ratio of dichlorophenyl-α-naphtylsilane to metalic mercury was $1:10^{-2}$.

Generally the condensation reaction proceeds according to the following scheme:



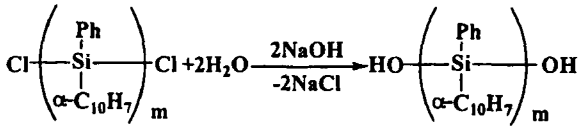
Where for the structure B : $m \approx 4$(I), 8(II), 15(III), 20(IV).

The oligomers I and II were partially reprecipated from toluene solution with anhydrous hexane. The yield of these compounds is about 62%. It was established that during this reaction intramolecular cyclization with formation cyclic phenyl-α-naphtylsilanes takes place besides the intermolecular condensation. We found it impossible to separate cyclosilanes ($m = 4 \div 6$) by distillation in vacuum ($p = 1 \div 2 \times 10^{-2}$ mmHg), because during the distillation the polymerization reactions of phenyl-α-naphtylcyclosilanes took place.

Oligomers III and IV too, were reprecipated from toluene solution by anhydrous hexane. Gel permeation analysis showed a monomodal character of the molecular weight distribution (Fig. 1). In Table I some physical-chemical properties of the synthesized oligomers are presented.

The synthesized oligomers are coffee color solid products highly soluble in aromatic solvents. The structure and composition of the synthesized oligomers were determined by means of functional and element analysis, by finding the molecular masses and by IR spectra. In the IR spectra of compounds I-IV one can observe the absorption bands for valence oscillation, characteristic for Si—Si (1000 - 1100 cm^{-1}), Si—C$_{aryl}$ (1000 and 1430 cm^{-1}), Si—Cl (490 cm^{-1}), C—H (3000 - 3080 cm^{-1}), CH=CH (3050 cm^{-1}) and also for monosubstituted benzole ring in the region (700,1600 cm^{-1}).

The hydrolysis reaction of α,ω-dichlorophenyl-α-naphtylsilanes in alkaline solution, in the presence of sodium hydroxide, was carried out in the temperature region $-5 \div -10°C$ and the corresponding α,ω-dihydroxyphenyl-α-naphtylsilanes has been obtained. The reaction proceeds according to the following scheme:



$$Cl\left(\underset{\alpha\text{-}C_{10}H_7}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}\right)_m Cl + 2H_2O \xrightarrow[-2NaCl]{2NaOH} HO\left(\underset{\alpha\text{-}C_{10}H_7}{\overset{Ph}{\underset{|}{\overset{|}{Si}}}}\right)_m OH$$

Where: $m = 4$(V), 8(VI), 15(VII), 20(VIII).

The oligomers V ÷ VIII were reprecipitated from toluene solution by anhydrous hexane. They are white solid products soluble in aromatic solvents. In the IR spectra of compounds V ÷ VIII the absorption bands at 490 cm^{-1}, characteristic for Si—Cl bonds, disappear and the absorption bands characteristic for Si—OH bonds appear at 3200 - 3400 cm^{-1}. Some physical-chemical properties and the yields of α,ω-dihydroxyphenyl-α-naphtylsilanes are presented in Table II.

As it is seen from Table II with the increase of the length of polysilane fragments the values of interchain distances, d_1 slightly rise.

For the purpose of the synthesis of polysilane-siloxane blockcopolymers a reaction of heterofunctional condensation (HFC) of α,ω-dihydroxy(dichloro)phenyl-α-naphtylsilanes with α,ω-dichloro(dihydroxy)dimethylsiloxanes, in 60% anhydrous solution

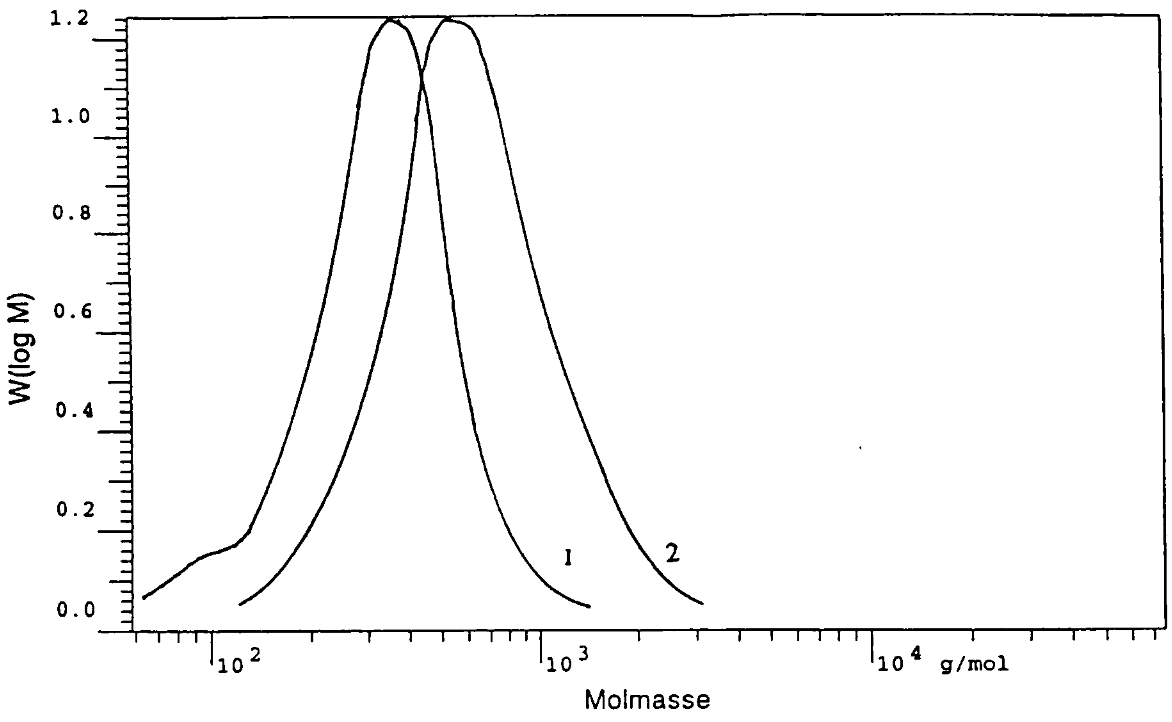


FIGURE 1 Gel permeation chromatography curves of α,ω-dichlorophenyl-α-naphtylsilanes. Where curve 1 corresponds to oligomer III and curve 2 corresponds to oligomer IV.

TABLE I Physical-chemical properties of α,ω-dichlorophenyl-α-naphtylsilanes

4	*Ratio* $RR'SiCl_2$ *: Na*	*Yield, %*	T_{melt} °C	$\overline{M}$*,**	*Cl%*
I	1:1,5	56	178-185	$\frac{720}{767}$	$\frac{9,85}{9,25}$
II	1:1,8	62	194-199	$\frac{2005}{1927}$	$\frac{3,54}{3,68}$
III	1:1,8	61	206-212	$\frac{3504}{3551}$	$\frac{2,02}{1,99}$
IV	1:2,0	57	262-270	$\frac{4680}{4711}$	$\frac{1,53}{1,50}$

* In the denominator there are calculated values in numerator experimental values.

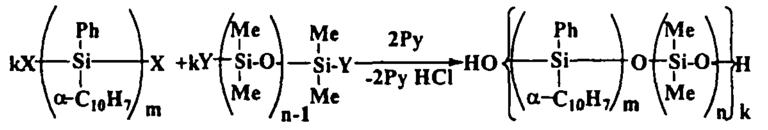
** Molecular weights have been determined by ebuliometric method by GPC (III, IV) and by %Cl end group analysis.

TABLE II Some physical-chemical properties of α,ω-dihydroxyphenyl-α-naphtylsilanes

					$\overline{M}$*		*OH%*	
No.	*Yield, %*	*Tmelt, °C*	η_{sp}, *1% solution, in toluene, at 25°C*	d_1, *Å*	*Calcul.*	*Found*	*Calcul.*	*Found*
1	2	3	4	5	6	7	8	9
V	82	60-62	0,03	10,72	962	975	3,53	3,49
VI	87	115-120	0,04	11,05	1890	1900	1,80	1,79
VII	89	127-131	0,04	11,05	3514	3550	0,97	0,95
VIII	92	144-149	0,04	–	4674	4500	0,73	0,74

* Molecular weights have been determined by ebuliometric methods for oligomers (V-VIII) and by OH end group analysis.

of toluene, in the presence of pyridine in 1:1 ratio of initial compounds at the temperature range 20 ÷ 25°C has been carried out. The reaction proceeds according to the following scheme:



Where: X = Cl, OH, Y = OH, Cl. $m \approx 4$, $n \approx 19$(IX), 40(X) $m \approx 8$, $n = 2$(XI), 6(XII), 19(XIII), 27(XIV). $m \approx 15$, $n = 2$(XV), 6(XVI), 19 (XVII), 27(XVIII). $m \approx 20$, $n = 2$(XIX), 6(XX), 19(XXI), 27(XXII).

After reprecipitation from toluene solution by methyl alcohol, the block-copolymers are obtained as coffee color solid systems, nicely soluble in organic solvents with $[\eta] = 0,1 \div 0,30$. The fractionation of copolymer XVII partially reprecipitated from toluene solution by methanol has been carried out. Five fractions were obtained. Element analysis of these fractions showed that they differred from each other only a little. This shows that during HFC the reaction of homofunctional condensation is unlikely and block-copolymers are obtained with regular arrangement of polyphenyl-α-naphtylsilane fragments in the macromolecular chain. The value of $[\eta]$ of fractionated polymer XVII in toluene solution is equal to 0,29 (its weight fraction is about ~28%) and most low molecular weight fractions give $[\eta] \cong 0.10$ (their weight fraction is 23%).

Some physical-chemical properties of the synthesized block-copolymers are presented in Table III. In ^{1}H NMR spectra of copolymer XVI one can observe a singlet signal for methyl protons with chemical shift at $\delta = 0{,}24$ ppm, which supports regular alternation of polysilane-siloxane blocks and is in conformity with the literature data [15].

A gel permeation chromatography analysis of some block-copolymers was carried out. As is seen from Figure 2 the copolymers has a monomodal molecular weight distribution with $\overline{M}_w \approx 21 \times 10^{-3} \div 58 \times 10^{-3}$ and the polydispersity changes from 1.4 to 2.1. An X-ray diffraction study was conducted on the synthesized block-copolymers.

As is seen from Figures 3 and 4, depending on the length of the rigid polyphenyl-α-naphtylsilane fragments (m) and the flexible dimethylsiloxane fragment (n) a block structure is realized in the copolymers (phase incompatibility). At small values of flexible dimethylsiloxane fragments and rigid polyphenyl-α-naphtylsilane fragments ($m \approx 4$) the copolymers occur as a one phase system. The maximum values of interchain distances are achieved at the small values of $n = 2$. In the diffraction patterns one can observe two diffraction maxima $2\theta^\circ = 8{,}25^\circ$ and $2\theta^\circ = 19{,}75 \div 20{,}5^\circ$, the first value corresponds to an interchain distance of $d_1 = 10{,}72$ Å. This maximum interchain distance is near the interchain distance of polyphenyl-α-naphtylsiloxane-dimethylsiloxane block-copolymers where the value is $d_1 = 10{,}90$ Å [14]. The second maximum at $2\theta^\circ = 19{,}75^\circ \div 20{,}5^\circ$ corresponds to $d_2 = 4{,}49 \div 4{,}33$ Å, which corresponds to both intra- and interchain atomic distances [16]. With an increase in the length of dimethylsiloxane chain to $n \geq 19$, flexible block properties start to appear and a two-phase system is obtained. As is seen from Figure 4, for block-copolymers with $n > 19$ the value of interchain distances decreases

TABLE III Some physical–chemical properties of polyphenyl-α-naphtylsilane-dimethylsiloxane block-copolymers

N	*Yield*, %	[η] *dl*/*g*	d_1,Å	T_g, °*C*	T_{melt} °*C*, T_{soft} °*C*	5% *mass losses*	*Residual mass*, %	*Elementary composition*, %		
								C	*H*	*Si*
IX	94	0,31	7,53	−123	–	300	31	$\frac{52{,}08}{52{,}45}$	$\frac{4{,}85}{4{,}31}$	$\frac{27{,}40}{27{,}04}$
X	95	0,30	7,53	−123	–	300	18	$\frac{44{,}46}{44{,}06}$	$\frac{7{,}38}{6{,}86}$	$\frac{31{,}56}{31{,}60}$
XI	93	0,25	10,72	–	+ 102 ÷ + 107	+ 360	32	$\frac{78{,}41}{78{,}04}$	$\frac{5{,}35}{5{,}01}$	$\frac{13{,}86}{13{,}43}$
XII	94	0,26	10,70	–	+ 100 ÷ + 103	–	–	$\frac{72{,}54}{71{,}97}$	$\frac{5{,}69}{5{,}23}$	$\frac{16{,}93}{16{,}62}$
XIII	95	0,29	10,70 – 8,04	−123	−45,3 + 110	+ 310	18	$\frac{60{,}77}{60{,}23}$	$\frac{6{,}40}{6{,}13}$	$\frac{23{,}06}{22{,}84}$
XIV	94	0,28	10,10 – 7,70	−123	−45,1 + 100	+ 320	13	$\frac{56{,}43}{56{,}12}$	$\frac{6{,}66}{6{,}34}$	$\frac{25{,}32}{24{,}94}$
XV	94	0,16	–	–	+ 118 ÷ + 122	+ 350	28	$\frac{79{,}03}{79{,}56}$	$\frac{5{,}27}{4{,}78}$	$\frac{13{,}06}{13{,}33}$
XVI	92	0,20	10,70	–	+ 103 ÷ + 110	+ 320	20	$\frac{76{,}75}{76{,}43}$	$\frac{5{,}48}{5{,}11}$	$\frac{14{,}92}{14{,}62}$
XVII	93	0,25	10,40 – 8,23	−117	−26, + 95	–	–	$\frac{68{,}05}{67{,}76}$	$\frac{5{,}99}{6{,}21}$	$\frac{19{,}42}{19{,}23}$
XVIII	94	0,27	10,70 – 8,04	−115	−50, + 104	–	–	$\frac{64{,}21}{64{,}11}$	$\frac{6{,}22}{6{,}10}$	$\frac{21{,}41}{21{,}69}$
XIX	93	0,29	10,72	–	+ 115 ÷ + 123	+ 410	54	$\frac{80{,}93}{80{,}66}$	$\frac{5{,}24}{5{,}65}$	$\frac{12{,}82}{13{,}30}$
XX	92	0,21	10,10	–	+ 120 ÷ +126	–	–	$\frac{78{,}11}{78{,}34}$	$\frac{5{,}41}{5{,}09}$	$\frac{14{,}27}{14{,}07}$
XXI	95	0,22	10,10 – 7,53	−120	−30, + 90	+ 400	48	$\frac{70{,}87}{70{,}40}$	$\frac{5{,}84}{5{,}61}$	$\frac{18{,}01}{18{,}42}$
XXII	96	0,23	10,10 – 7,70	−120	−45, + 85	+ 370	13	$\frac{67{,}44}{67{,}11}$	$\frac{6{,}04}{6{,}34}$	$\frac{19{,}77}{20{,}45}$

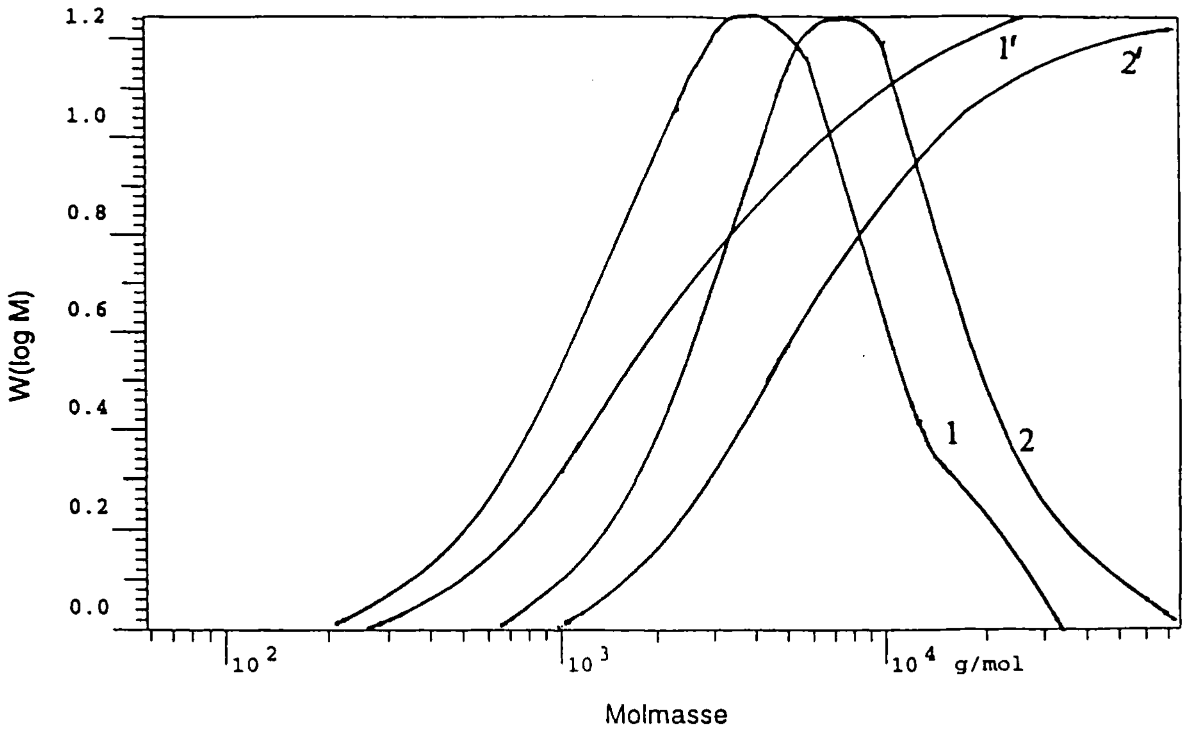


FIGURE 2 Gel permeation chromatographic curves of polyphenyl-α-naphtyl-dimethylsiloxane block-copolymers. Where curve 1 and 1′ corresponds to copolymer XII, and curve 2 and 2′ corresponds to copolymer XVII.

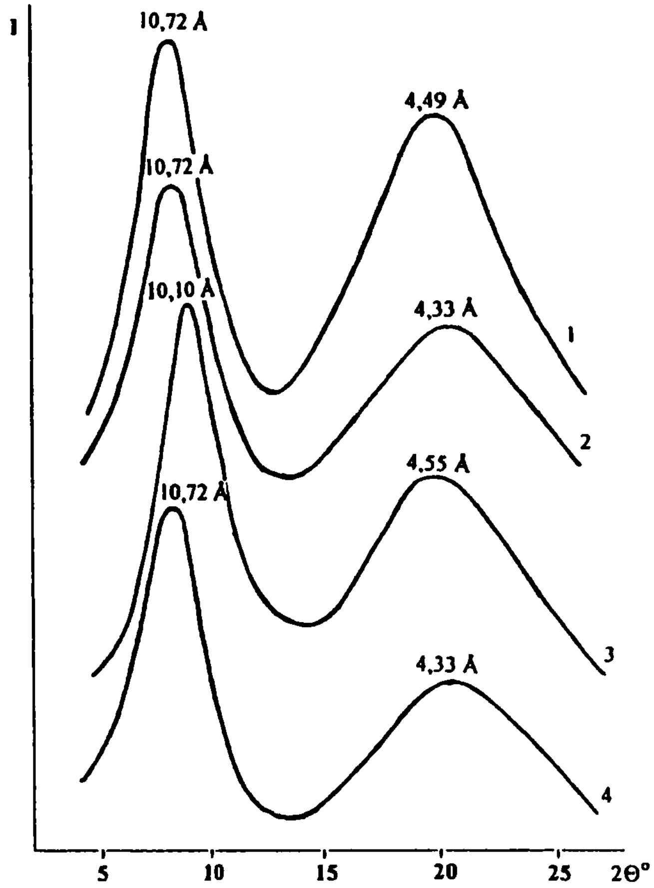


FIGURE 3 X-ray diffraction patterns of polyphenyl-α-naphtyl-dimethylsiloxane block-copolymers. Where curve 1 corresponds to copolymer XIX, curve 2 corresponds to copolymer XII, curve 3–XX and curve 4 corresponds to copolymer XI.

and consists of $d_1 = 10{,}10\,\text{Å}$ and on the diffraction pattern a third diffraction maximum appears in the range $d_1 = 7{,}70 \div 8{,}23\,\text{Å}$, which corresponds to the interchain distance in the linear polydimethylsiloxane. The appearance of the third diffraction maximum in such length values of dimethylsiloxane links (n) shows that we deal with two-phase systems. Compared with polyphenyl-α-naphtylsiloxane-dimethylsiloxane block-copolymers [14], the first maximum of interchain distances characteristic for rigid polyphenyl-α-naphtylsilane fragments decreases, but the value d_1 of the synthesized block-copolymers,

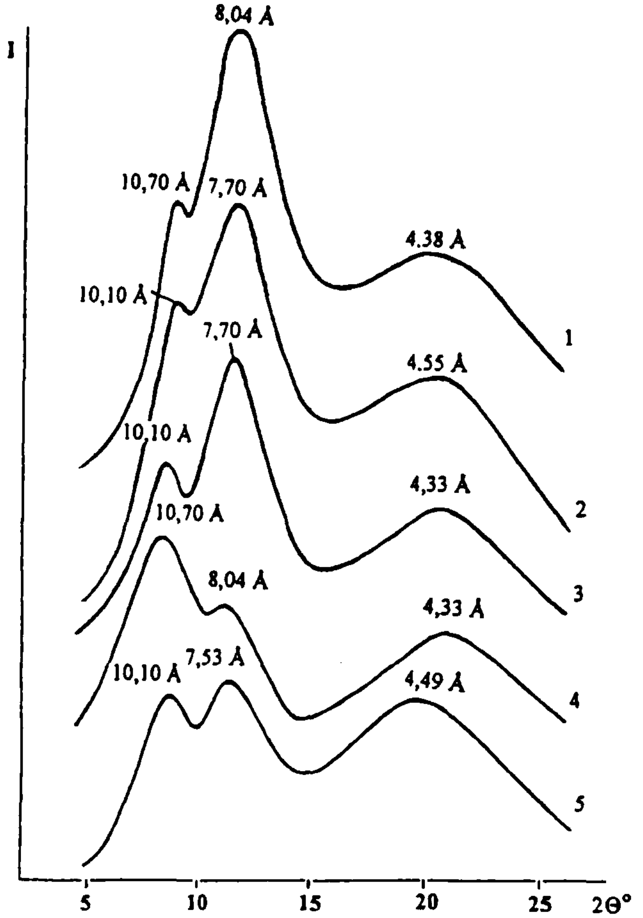


FIGURE 4 X-ray diffraction patterns of polyphenyl-α-naphtyl-dimethylsiloxane block-copolymers. Where curve 1 corresponds to copolymer XVIII, curve 2 corresponds to copolymer XXII, curve 3 corresponds to copolymer XIV, curve 4 corresponds XIII and curve 5 corresponds to copolymer XXI.

characteristic of flexible dimethylsiloxane fragments is a bit larger than for polyphenyl-α-naphtylsiloxane-dimethylsiloxane block-copolymers [14]. It is necessary to note that with the increase of *n*, the intensity of the third maximum rises. Therefore, during the formation of two phase systems when *n* has definite values the segregation processes take place separately for rigid polyphenyl-α-naphtylsilane fragments as well as for dimethylsiloxane fragments, resulting in the formation of domains of rigid and flexible blocks separately and which are divided as two separate phases. These results conform with earlier published data [14, 17], where phenyl-α-naphtylsiloxane fragments are separated as independent domains in phenyl-α-naphtylsiloxane-dimethylsiloxane block-copolymers.

The synthesized block-copolymers were studied by a differential scanning calorimetric method. At small values of the length of rigid polyphenyl-α-naphtylsilane ($m \approx 4$) fragments and dimethylsiloxane chain ($n < 19$) the copolymers appeared as a one phase system with a single softening temperature. With the increase in the length of dimethylsiloxane links ($n \geq 19$) and the rigid polyphenyl-α-naphtylsilane fragments ($m > 4$) one can observe two glass transition temperatures in the DSC curves, Figure 5, in the range a $T_g \approx -120°C \div -115°C$ characteristic for linear flexible dimethylsiloxane chains and a $T_g \approx 80°C \div 105°C$ characteristic for rigid polyphenyl-α-naphtylsilane fragments. In Figures 6 and 7 one can observe two phase transitions: crystallization in the temperature range $T_{cryst} \approx -70°C \div -100°C$ and melting temperature (T_{melt}), which is characteristic for dimethylsiloxane blocks, in a temperature range of $T_{melt} \approx -27°C \div -50°C$. As is known from the literature [18, 19], the presence of any chemical inclusions in the polydimethylsiloxane chain (pendant groups other than methyl, branching sites) results in a loss of the ability to crystallize at distances of 30 Si—O links between the chain inclusions and the copolymers studied there do not crystallize at lengths of $n \leq 25$. But in our case the crystallization of block-copolymers can be observed from the length of dimethylsiloxane chain $n \geq 19$ (see Figs. 6 and 7). Curves 1 and 2 in Figures 6 and 7 showed phase transition at the first and second heating scans. Curve 3 in both Figures 6 and 7 showed phase transition at the cooling scans. In both cooling curves, in the range $-25°C \div -50°C$, there is indication of the phase transition characteristic of the melting temperature of methylsiloxane blocks. By comparing the DSC results with the thermomechanical properties of polyphenyl-α-naphtylsiloxane-dimethylsiloxane block-copolymers it is observed that melting temperature characteristic of dimethylsiloxane blocks in both block-copolymers has approximately the same values.

A thermogravimetric investigation of synthesized block-copolymers have been carried out. As is seen from Figures 8–10 the

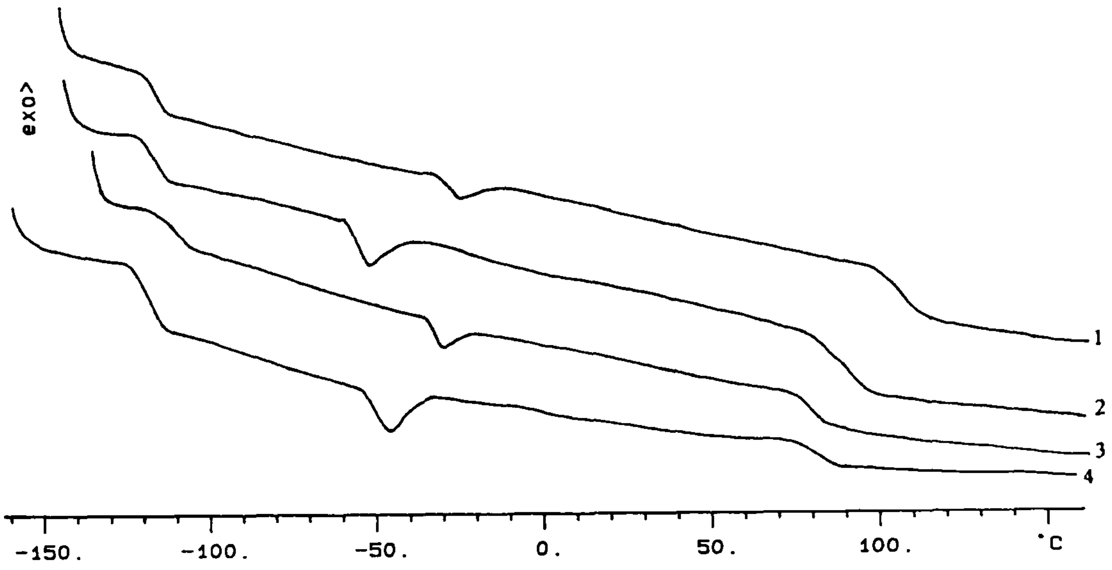


FIGURE 5 DSC first heating scans of polyphenyl-α-naphtyl-dimethylsiloxane block-copolymers. Where curve 1 corresponds to copolymer XVII, curve 2–XVIII, curve 3–XXI and curve 4–XXII. (Scanning rate 10°C min^{-1}).

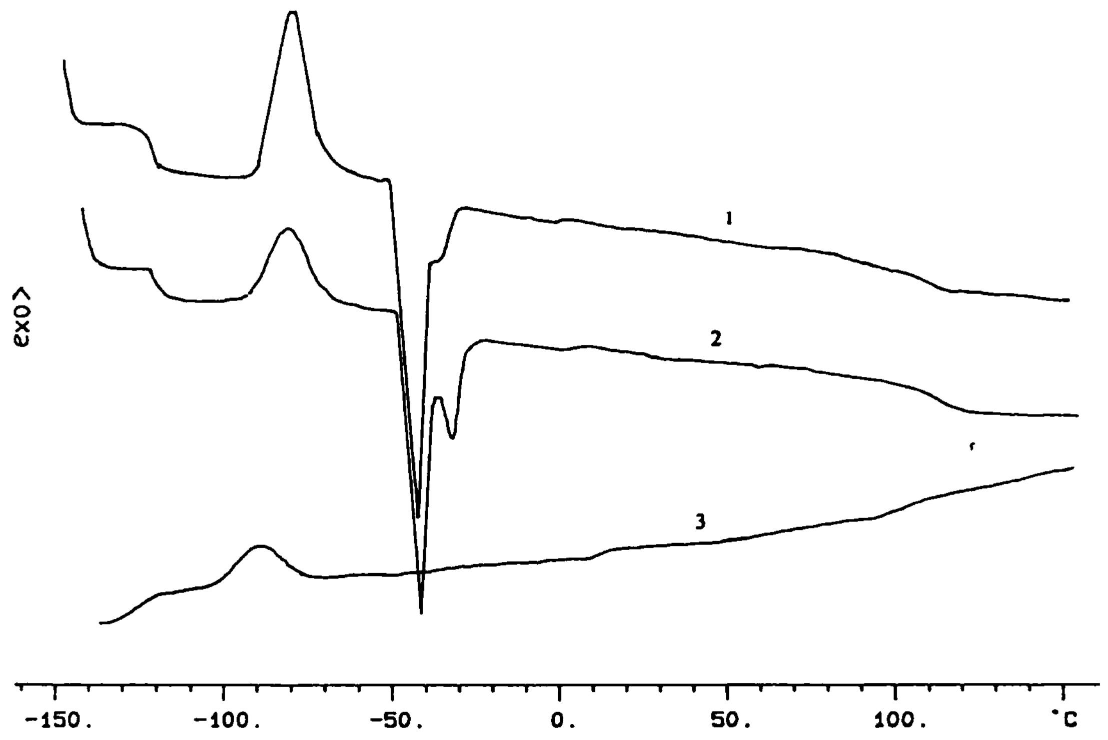


FIGURE 6 DSC thermograms of the polyphenyl-α-naphtyl-dimethylsiloxane block-copolymer XIII. Where curve 1 corresponds to first heating scans, curve 2 corresponds to second heating scans and curve 3 corresponds to cooling scans. (Scanning rate 10°C min^{-1}).

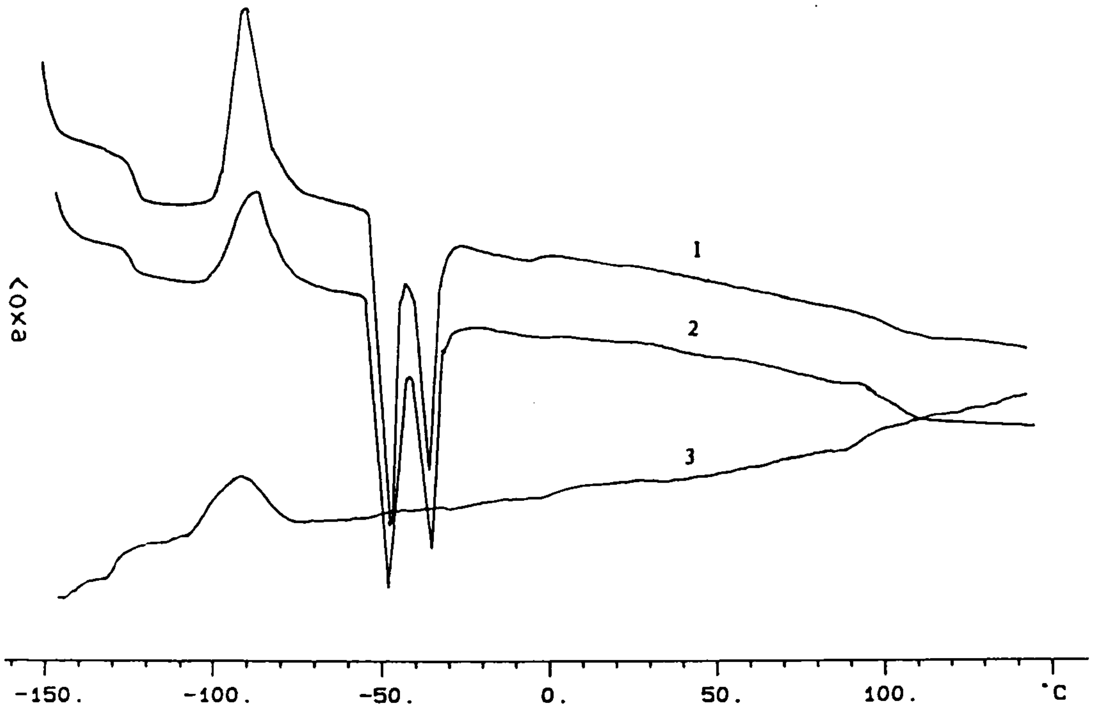


FIGURE 7 DSC thermograms of the polyphenyl-α-naphtyl-dimethylsiloxane block-copolymer XIV. Where curve 1 corresponds to first heating scans, curve 2 corresponds to second heating scans and curve 3 corresponds to cooling scans. (Scanning rate 10°C min^{-1}).

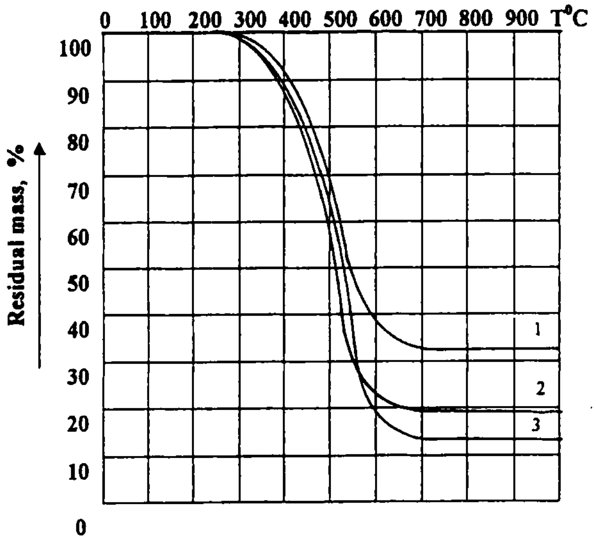


FIGURE 8 Thermogravimetric curves of polyphenyl-α-naphtyl-dimethylsiloxane block-copolymers. Where curve 1 corresponds to copolymer XI, curve 2 – XIII and curve 3-XIV.

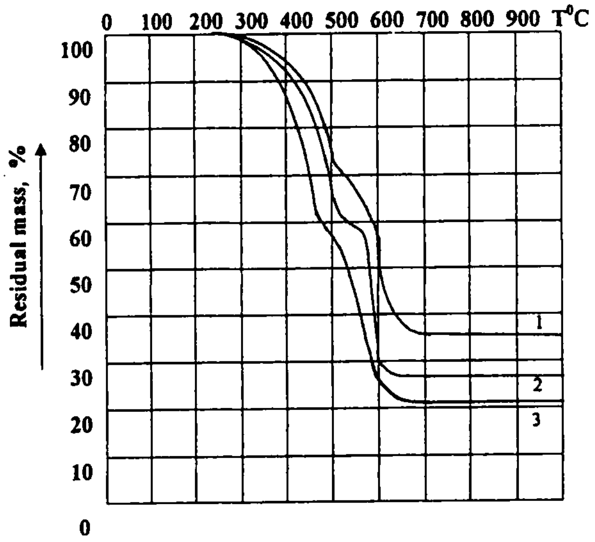


FIGURE 9 Thermogravimetric curves of polyphenyl-α-naphtyl-dimethylsiloxane block-copolymers. Where curve 1 corresponds to copolymer XV, curve 2-XVII and curve 3-XVIII.

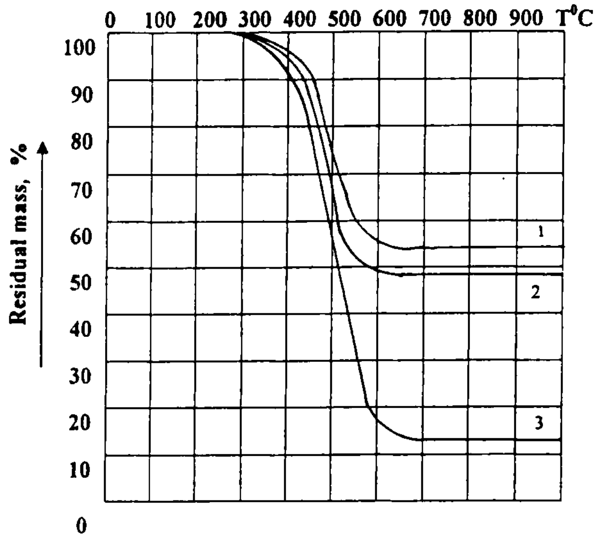


FIGURE 10 Thermogravimetric curves of polyphenyl-α-naphtyl-dimethylsiloxane block-copolymers. Where curve 1 corresponds to copolymer XIX, curve 2–XXI and curve 3–XXII.

block-copolymers are characterized by higher thermal-oxidative stability compared with linear polydimethylsiloxane. 10% mass losses for polysilane–siloxane polymers are observed at 370°C–450°C and in addition with an increase of the part of phenyl-α-naphtylsilane fragments in the chain, the thermal-oxidative stability of block-copolymers rises. This is in agreement with the conclusion that the insertion of more rigid fragments in polydimethylsiloxane chain hinders the cyclic depolymerization [20]. On the other hand, it may be explained by the high resistance of phenyl groups to oxidation as well as their inhibiting effect on oxidation of methyl groups [21]. The main thermal destruction process proceeds over the range 450°C–700°C, and above 700°C curves of mass losses remain constant. With an increase of the length of dimethylsiloxane chain, the amount of char residue decrease. The synthesized polysilane–siloxane polymers and polyphenyl-α-naphtylsiloxane-dimethylsiloxane block-copolymers [17] are characterized approximately by the same thermal-oxidative stability.

Thus, for the first time polyphenyl-α-naphtylsilane-dimethylsiloxane block-copolymers were synthesized by us and it was shown that polyphenyl-α-naphtylsilane fragments behave as polyphenyl-α-naphtylsiloxane rigid blocks. With the insertion of phenyl-α-naphtylsilane fragments in dimethylsiloxane chain the main thermal destruction process proceeds at 80 – 100°C higher than in unblocked polydimethylsiloxane polymers.

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